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(21) International Application Number: PCT/RU98/00028 (22) International Filing Date: 10 February 1998 (10.02.98) (30) Priority Data: 97112750 6 August 1997 (06.08.97) RU (71) Applicant (for all designated States except US): OBSHESTVO S OGRANICHENNOI OTVETSTVENNOSTYU PROIZ VODSTVENNO-KOMMERCHESKAYA FIRMA ATLANTIS-PAK [RU/RU]; ul. B.Sadovaya, 188, Rostov-na-Donu, 344022 (RU). (72) Inventors; and (75) Inventors/Applicants (for US only): BORODAIEV, Sergei Vasilievich [RU/RU]; ul. Moskovskaya, 19-3, Rostov-na-Donu, 344008 (RU). DAVYDENKO, Oleg Vladimirovich [RU/RU]; pr. Kosmonavtov, 32a-12, Rostov-na-Donu, 344113 (RU). DAVYDENKO, Alexandr Vladimirovich [RU/RU]; ul. V.Panovoi, 32/1-91, Rostov-na-Donu, 344112 (RU). RYZHENKO, Sergei Petrovich [RU/RU]; ul. Komarova, 30/1-27, Rostov-na-Donu, 344113 (RU). (74) Agent: STOYACHENKO, Igor Leonidovich; ul. Miklukho-Maklaya, 65-4-34, Moscow, 117342 (RU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A HOSE FILM ON THE BASIS OF POLYAMIDES (57) Abstract <p>The invention concerns hose films on the basis of polyamides which can be used for production of hose films orientated in two axes usable in manufacture of paste-like and viscous products which may be subjected to heat treatment in temperature range 70-125 °C. A hose film on the basis of polyamides, including polyamide 6, aliphatic copolyamide, aromatic polyamide, containing hexamethylenediamine and terephthalic acid units and a copolymer, including olefin units, is claimed which additionally contains an ionomer resin. As aliphatic copolyamide, it contains a copolymer of polycaprolactam, polyhexamethylenediamine and adipic acid. As copolymer including olefin units, it contains a mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids. The components are present in following amounts (weight parts): Polyamide 6: 77-83; copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid: 7-13; aromatic polyamide, containing hexamethylenediamine and terephthalic acid units: 3-7; ionomer resin: 3-6; mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids: 0.1-5.</p>		

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A HOSE FILM ON THE BASIS OF POLYAMIDES

Branch of the invention

The invention concerns to hose films on the basis of polyamides and can be used for production of the orientated in two axis hose film to be used in manufacture of paste like and viscous products which may be subjected to heat treatment in temperature range 70-125° C. The invention concerns in particular, to manufacturing of a hose film for production of sausages, and also of processed cheeses, packed in the form of sausage, which are packing up as a rule, in softened state or viscous-liquid state.

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Background of the invention

There is the plenty of kinds of a polymeric film, used in manufacture of paste like or of packed up processed products.

Composition for reception of a coat for sausages includes polycaprolactone with molecular weight in the range 1000-4000, 1,6-hexamethylenediisocyanate and 1,4-buthanediol in the following ratio of listed components (weight parts): 24-30, 50-40, 24,84-27,0 (SU, A1, 1034597).

For production of the coat the components of a composition heat up to 60-50°C with subsequent increase of temperature up to 240°C. The received product is poured on potytetrafluorethylene film. After 5 hours the plate poured off is granulated, heated up again and extruded.

Nevertheless it is necessary to carry out a previous treatment of a known composition before extrusion, which require a lot of time. Besides the film has a thickness no less than 0,05 mm and is suitable only for using with special machines. Moisture content in the coat is 0,03 %, it is enough for detention of the coat in the process of coating in a stretched and elastic condition, but during cooking the contents of water in the coat increased so, that it negatively influences mechanical characteristics of the coat.

The coats on the basis polyamide may be better subjected to stretching and shrinkage, they have high durability, and also are suitable not only for machine filling but also hand-operated filling.

It is known a film, used in manufacture of paste like food products, in particular of sausages and cheese, containing at least one aliphatic polyamide

and at least one ionomer resin and/or at least one modified copolymer of ethylene and of vinylacetate (DE, A1, 2850181).

As polyamides in the known hose film the polycaprolactam, polyaminoenanthamide, polyhexamethylenedipamide and/or polyhexamethylenesebacinamide as separate substances or as a mixture each with other, and also copolymers of above polyamides and of polyaminoundecaneamide or polylaurinelactam are used.

The thickness of received hose film is about 0,050 mm, that is satisfactory only for machine filling; permeability for water is in a range 12-28 g/m³ in a day, and permeability for oxygen is about 15 up to 30 cm³/m² day bar.

This film is manufactured as follows: the components are mixed, plasticized at 260° C and moulded, preferable by extrusion of a sleeve with blowing. Then biaxial stretching with multiplicity of the lengthways and across stretching in a range from 1:1,5 up to 1:4 is carried out. Then the sleeve is thermofixed for stabilization of the sizes.

However the known technical decision does not allow to receive more thin films for hand-operated filling and to provide strength of the film necessary at cooking. On cutting of the coat its propensity to breaks was indicated. For preparation of cooked sausages a forcemeat should filled in this coat under significant pressure about 0,3-0,6 bars. For hand-operated filling of sausage forcemeat, during which pressure of the filling is insignificant, such coat hardly can be used, as after terminating of the working cycle of preparation of sausages folds or fractures will be formed

The closest known technical decision to the claimed one is a hose film on a basis of polyamides, used in manufacture of paste like and viscous food products (sausage coat), including polyamide 6, aliphatic copolyamide, aromatic polyamide, containing hexamethylenediamine and terephthalic acid units, and copolymer including olefin units (EP, A1, 0722664).

This hose film contains (weight. %):

a) polyamide 6

b) aliphatic polyamide (5-50 % of general weight of all polymers in a layer) As the aliphatic copolyamide is used the copolyamide with units of ϵ -caprolactam,

of hexamethylenediamine and of azelaic acid (polyamide 6/6,9) and/or polyamide 6,12 as copolyamide from hexamethylenediamine and dodecanic acid,

5 B) up to 20% of aromatic polyamide, partially aromatized by hexamethylenediamine and terephthalic or isophthalic acids units (PA 6-T or PA 6-T),

c) up to 20 % of copolymer having olefin units of polyolefin, modified by carboxy groups, in particular of copolymer of ethylene and of methacrylic acid.

The hose film may involve dyes and/or pigments in few amounts.

10 The manufacturing of monolayer and multilayer sausage coat includes mixturing and melting at the temperature about 240° C of components of the mixture in special extruder until producing of a homogeneous melted mixture, extrusion of the latter through ring injectors with blowing, moulding of an integral sleeve, which stretched then in longitudinal and cross directions under
15 air pressure. A received film is fixed by additional heat treatment.

The hose film received according to the known technology (prototype) gives shrinkage from 5 up to 25 % (at 80° C) in share and cross directions, it has thickness of 0,033-0,056 mm, can be manufactured as multilayer. Water permeability of the sausage coat changes from 11,5 up to 13,1 g/m a day, and
20 oxygen permeability varies from 13,6 up to 18,5 cm³/m² day bar.

Multilayer hose film contains as a minimum one layer of the mentioned above polyamide mixture. Other layers consist mainly from polyamides (for example, polyamide 6), polyamide mixtures, polyolefins (for example, polyethylene or polypropylene), also from polyolefins, containing binding
25 functional groups. Besides the layers can be manufactured from copolymers with units of ethylenenonsaturated monomers (for example, vinylacetate, vinyl alcohol, acrylic and methacrylic acid), and also of vinylidenchloride or acrylonitrile copolymers, of ionomer resins or of mixtures of above named polymers.

30 A coat usually consists of 3- 5 layers. Such coat may be manufactured by coextrusion through ring injectors, which are specially designed according to quantity of layers.

Multilayer coats being compared with monolayer show higher water and vapour permeability and permeability for oxygen.

There is a lack both of monolayer and of multilayer hose films, claimed in EP 0722664. It is their rather high water and vapor permeability and permeability for oxygen of air, these parameters are of priority for ready sausage products, as they define a safety of ready product and loss of its weight. Moreover, the durability of a coat for viscous products and sterilized sausages, requiring stability under the technological rules on the temperature up to 125° C, is insufficient high.

Summary of the invention

The problem to be solved by the invention consists in creation of a hose film to be used in manufacture of paste like and viscous food products, having lower water and vapour permeability and permeability for oxygen, and also having increased strength characteristics under heat treatment.

The problem is solved by the claimed invention.

A hose film on the basis of polyamides, including polyamide 6, aliphatic copolyamide, aromatic polyamide, containing hexamethylenediamine and terephthalic acid units and copolymer, including olefin units, according to the invention, additionally contains ionomer resin, as aliphatic copolyamide it contains copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid, and as a copolymer including olefin units it contains a mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids with the following ratio of components (weight parts):

	Polyamide 6	77- 83
25	Copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid	7-13
	Aromatic polyamide, containing hexamethylenediamine and terephthalic acid units	3-7
	Ionomer resin	3-6
30	Mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids	0,1-5

The hose film may contain zinc salt of copolymer of ethylenemethacrylic acid as ionomer resin.

In the claimed film hose the copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid may be used (polyamide 6/6,6 with elements of the formulas $-N-(CH_2)_5-CO-$, $-N-(CH_2)_6-NH-$, $-CO-(CH_2)_4-CO-$) with quantity of parts of monomers accordingly 85, 7,5 and 7,5 weight %.

The hose film may contain as a mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids the mixture with the contents of graft units from 0,3 up to 0,9 weight %

The hose film may be carried out as multilayer, and at least one layer has the following composition: (weight parts):

Polyamide 6	77- 83
Copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid	7-13
Aromatic polyamide, containing hexamethylenediamine and terephthalic acid units	3-7
Ionomer resin	3-6
Mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids	0,1-5

In such embodiment of the invention in the hose film other layers of multilayer hose film are carried out from polyamides, or of polyamide mixtures, or of polyolefins, or of polyolefins containing connecting functional groups, or of copolymers with units of ethylenenonsaturated monomers, or of copolymers of vinylidenechloride or acrylonitrile or of ionomer resins or of mixtures of these polymers.

Detailed description of the invention

The hose film can contain if necessary, additional dyes, pigments and/or auxiliary substances of processing. The share of these components rather small, so the basic characteristics of the film remain constant.

Below the components of the hose film are designated as follows:

1) - polyamide 6,

- 2) - copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid,
3) - aromatic polyamide, containing units of hexamethylenediamine and of terephthalic acid,
5 4) - ionomer resin
5) - mixture of graft copolymers on the base of derivatives of carboxylic and of polycarboxylic acids.

As graft copolymers for example, acrylic polymer with graft units of maleic anhydride, linear polyethylene of low density with graft units of maleic anhydride and ethylenepropylene rubber with graft groups of maleic anhydride
10 are used.

Mixture of graft copolymers on the basis of derivatives of carboxylic and of polycarboxylic acids allows to enter into structure of the hose film some other, more easier processed and more accessible copolymers, for example,
15 copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid instead of copolymer of polycaprolactam and polyhexamethylenediamine and azelaic acid used at manufacturing of known hose films

Due to preferable use of set of components of the hose film in the ratio: from 79 to 81 % of total weight of a component 1), from 9 up to 11 % of a component 2), from 4 up to 6 % of a component 3), from 4 up to 5% of a component 4), from 0,5 up to 1,5 % of a component 5), the properties are reached which have not both separate components of the film and known structures of hose films, namely: higher water and vapour permeability and permeability for oxygen, and besides, the film is thermostable up to 125° C and
25 is not subjected to breaks at thermal processing (cooking).

Example 1.

A mixture from

- 1) 80 weight parts of usual granulated polycaprolactam (polyamide 6) with relative viscosity 4 (measured for 1 g of granulated polycaprolactam in 100 ml of 96 % sulfuric acid at 20° C)
30 2) 10 weight parts of copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid (polyamide 6/6,6) with relative

viscosity 3,32 (measured for 1 g of granulated polycaprolactam in 100 ml of 96 % sulfuric acid at 20°C).

3) 5 weight parts of aromatic polyamide with units of hexamethylenediamine and of terephthalic acid (Selar PA 3426, Du Pont de Nemour Inc.) (melting index 90 g for 10 min at 275°C and loading of 10 kg).

4) 4 weight parts of ionomer resin - copolymer of ethylene and of methacryl acid with 2-20 % of methacryl acid having melting index 2,5 g for 10 min at 190° C and 2,16 kgs of a loading and with kind of an ion - Zn (Serlin -N 1652, DuPont).

5a) 0,5 weight parts of acrylic polymer with graft units of maleic anhydride (Fuzabond A, DuPont) (melting index 3,5 g for 10 min at 280°C and 2,16 kgs of loading).

5b) 0,5 weight parts of linear polyethylene of low density with graft units of maleic anhydride (Fuzabond E, DuPont) (melting index 3,0 g at 280° C for 10 min. and 2,16 kgs of a loading).

Components 1-5 in the above specified quantities are carefully mixed and loaded into the bunker of an extruder where the mixture of granules is homogenized at 255° C up to receiving of homogeneous melt. The melt is submitted on the ring head of extruder, on passage through which a primary sleeve is produced. Leaving from the extruder a primary sleeve is sharply cooled and then is heated up for plastification. Then it undergo to biaxial stretching which is carried out by compressed air. Then the moulded sleeve is directed to the furnace for thermofixation where there is the process of its stabilization. Then a sleeve is cooled, then it is submitted on the receiver, where it is reeled up on a fiber drum in a combined form.

Example 2.

To receive a multilayer hose the following polymeric mixtures are applied.

Mixture 1;

1) 80 weight parts of usual granulated polycaprolactam (polyamide 6) (as in the example 1)

- 2) 10 weight parts of copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid (polyamide 6/6,6) (according to example 1)
- 3) 5 weight parts of aromatic polyamide with units of hexamethylenediamine and of terephthalic acid (according to example 1)
- 4) 4 weight parts of ionomer resin - copolymer of ethylenemethacrylic acid with 2-20 % of methacrylic acid (according to example 1)
- 5a) 0,5 weight parts of acrylic polymer with graft units of maleic anhydride (according to example 1).
- 56) 0,5 weight parts of linear polyethylene of low density with graft units of maleic anhydride (according to example 1)

Mixture II:

70 weight parts of polyethylene of low density with melting index 0,2 g for 10 min at 190° C and 2,16 kgs of a loading and 30 weight parts of linear polyethylene of low density modified by maleic anhydride with melting index 3 g for 10 min at 190°C and loading of 2,16 kgs.

Mixture III:

The mixture III is prepared similarly to mixture 1. Mixtures 1, II, III are plasticized in three single-screw extruders at 240°C until producing of homogeneous alloys, then they are fed to 3-layer ring injectors and are coextruded in a sleeve. The sleeve is processed in oriented in two axis and thermofixed hose film.

At general thickness of the film of 0,055 mm the layers have the following thickness:

- External layer (mixture 1): 0,030 mm
- Average layer (mixture II): 0,015 mm
- Internal layer (mixture III): 0,010 mm.

Examples 3-10 of compositions of the hose film are brought in Table 1.

Table 1.

Compo nents	N of examples							
	3	4	5	6	7	8	9	10
1)	80	80	80	80	78	82	77	80
2)	10	10	10	10	11	8	12	10
3)	5	5	5	5	5	4	7	5
4)	4	4	4	4	4	5	3	5
5a)	1	-	3	-	1	0,5	0,5	-
5b)	-	1	-	4	1	0,5	0,5	-

Properties of claimed hose films according to used compositions of examples 1-10 are submitted in table 2.

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Table 2

Technological properties of the coat (unit of measurements)	Examples									
	1	2	3	4	5	6	7	8	9	10
Durability on break, mPa										
Lengthways	60	70	40	40	50	50	60	60	55	45
Across	120	120	100	100	105	105	110	110	115	100
Relative lengthening at break, %										
Lengthways	160	180	200	200	190	190	170	160	160	200
Across	60	70	80	80	80	80	70	60	65	90
Water and vapor permeability g/m ² atm	10	2,8	28	30	28	24	18	14	16	34

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Permeability on O ₂ cm ³ /m ² atm	12	5,6	34	30	30	26	20	14	18	38
Thermostability °C	125	125	95	95	95	95	125	125	120	90
Durability on cooking										
80° C	0,1	0,1	0,5	0,4	0,3	0,3	0,1	0,1	0,15	0,5
125° C	0,15	0,15	0,7	0,5	0,4	0,4	0,2	0,3	0,2	0,7

Note:

The data are brought for a film by thickness of 0,04 mm. Conditions at tests: On items 1,2 V = 50 mm/min, V - speed of stretching, on items 3,4 during 24 hours at 23°C and relative humidity of air 80 %; on item 5 during 4 hours, on item 6 in water at 80°C with and 125° C, percent on 1000 sausage sticks.

The hose film produced according to the invention meets the requirements, necessary for use, in particular in manufacture of cooked sausages and of processed cheeses. The thickness of a film for machine filling of sausage forcemeat is 0,037-0,040 mm, for hand-operated filling it is 0,030-0,033 mm.

The hose film remains rather strong, also at high temperatures about up to 125°C it has large elasticity and it is soft to the touch, adjoins to contents even after complete cooling, will not practically lead to precipitation of jelly and of fat between sausage forcemeat and coat; its durability at filling and accuracy of calibre of sausages, made in such environments, does not decrease. There is no adhesion of food products to the hose film.

Distinctive feature of invented hose film is its low water- vapor- and oxygen permeability, that defines a high degree of safety of a ready product (ability to oxidize and loss of weight), and also its thermostability.

The durability of the coat is kept during heat treatment, percent of sausage sticks spoiled at cooking is no more than 1 % on 1000 ready sticks.

Industrial application

This invention may be used most effectively in the industry of production of auxiliary materials for food industry

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CLAIMS

1. A hose film on the basis of polyamides, including polyamide 6, aliphatic copolyamide, aromatic polyamide, containing hexamethylenediamine and terephthalic acid units and copolymer, including olefin units, characterized in that it additionally contains ionomer resin, as aliphatic copolyamide it contains copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid, and as a copolymer including olefin units it contains a mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids with the following ratio of components (weight parts):

10	Polyamide 6	77-83
	Copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid	7-13
	Aromatic polyamide, containing hexamethylenediamine and terephthalic acid units	3-7
15	Ionomer resin	3-6
	Mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids	0,1-5

2. The hose film on the basis of polyamides according to claim 1, characterized in that as ionomer resin it contains zinc salt of copolymer of ethylenemethacrylic acid.

3. The hose film on the basis of polyamides according to claim 1, characterized in that as a copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid it contain the copolymer with quantity of parts of monomers units accordingly 85, 7,5 and 7,5 weight. %.

25 4. The hose film on the basis of polyamides according to claim 1, characterized in that as a mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids it contain the mixture with the contents of graft units from 0,3 up to 0,9 weight %

5. The hose film on the basis of polyamides according to claim 1 characterized in that it is carried out as multilayer, and at least one layer has the following composition: (weight parts):

30	Polyamide 6	77-83
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	Copolymer of polycaprolactam and of polyhexamethylenediamine and of adipic acid	7-13
	Aromatic polyamide, containing hexamethylenediamine and terephthalic acid units	3-7
5	Ionomer resin	3-6
	Mixture of graft copolymers on the basis of derivatives of carboxylic and polycarboxylic acids	0,1-5

6. The hose film on the basis of polyamides according to claim 5,
characterized in that other layers of multilayer hose film are carried out of
10 polyamides, or of polyamide mixtures, or of polyolefins, or of polyolefins
containing binding functional groups, or of copolymers with units of
ethylenenonsaturated monomers, or of copolymers of vinylidenechloride or of
acrylonitrile, or of ionomer resins or of mixtures of these polymers.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/RU 98/00028

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A22C13/00 C08L77/00 B32B27/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A22C C08L B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 722 664 A (HOECHST AG) 24 July 1996 cited in the application see claims; examples ---	1-6
A	EP 0 467 039 A (HOECHST AG) 22 January 1992 see page 4, line 43 - page 5, line 54; claims ---	1-8
A	EP 0 758 527 A (WOLFF WALSDRODE AG) 19 February 1997 see claims; examples ---	1-6
A	DE 28 50 181 A (BECKER & CO NATURINWERK) 29 May 1980 cited in the application see claims; examples -----	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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